An optical Chemical Sensor Based on polymer Swelling for pH and Metal Ions Determination

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1.1 Chemical sensors

Chemical sensors constitute new analytical devices that provide experimental response related to the quantity of a chemical species. These devices are designed to operate in a continuous and reversible fashion in real time. The sensor may be constructed to monitor a specific analyte present in a variety of sample matrices, including liquids, and gases[1,2].

Chemical sensors consist of chemical recognition phases coupled to transduction elements[1]. The chemical recognition phase interacts with the analyte of interests and is detected by the transduction element. Typically, it converts current, potential, or light intensity into an electrical signal. The electrical signal is proportional to the concentration of the analyte in the sample being measured. A general construction principle of a chemical sensor is illustrated in figure 1.

To achieve good chemical sensors, they should have a variety of aspects such as high selectivity only to analyte in question, high sensitivity, long lifetime, short response time, ruggedness, stability, reliability, inexpensive,

small, simple to operate, reversible, easily calibrated, and can analyze nondestructively, rendering accurate information in a short time[3]. They are electrically passive, and can safely be used in vivo[10]. The signal is not subject to electrical interference. Light can be transmitted through fibers over long distances, the fibers are mechanically flexible[11].

1.1.1 Selectivity

Selectivity can be simply defined as the sensors ability to respond to one particular analyte of interest in the presence of other analytes. The sensing elements are constructed to provide selective measurement of analyte based upon its chemical reactivity, electrical, mass, or optical properties. The use of chemometric and pattern recognition techniques in combination with arrays of sensors is a strategy has been used successfully to overcome the lack of selectivity of individual sensors [3].

The selectivity is the most important parameter associated with a chemical sensor because it largely determines the accuracy of the analytical method. Since selectivity is always limited, all chemical sensors are prone to report higher concentration than a sample actually contains[4]. In the environmental field, this positive error can be considered as a safety margin

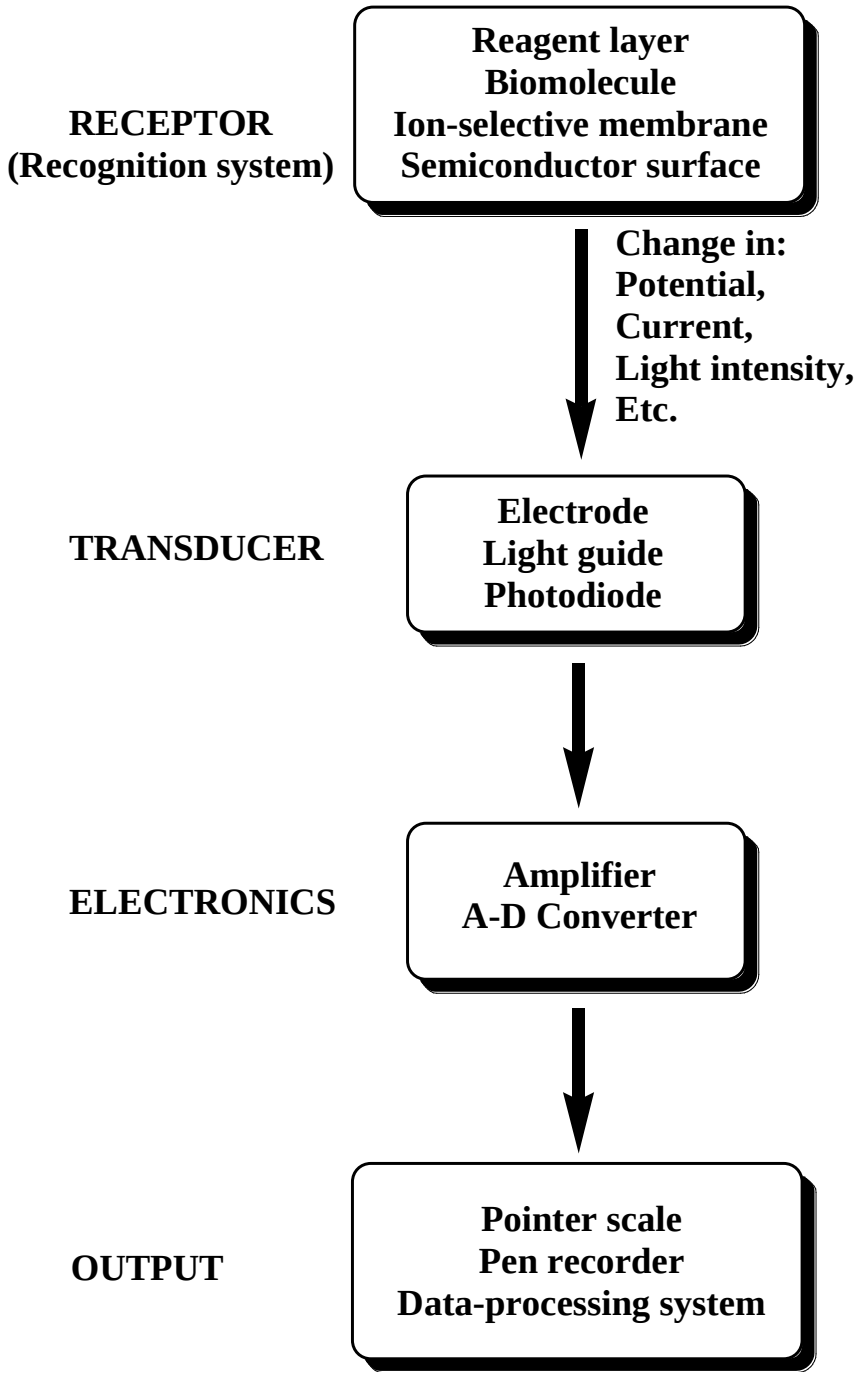


Figure 1.1: Generalized scheme of the main elements of a sensor.

if relevant interferents are also present[4]. Over the past decade; the possibility of selectivity and quickly sensing of a specific analyte with optical fibers has been the center of much research[3].

1.1.2 Sensitivity

The sensitivity of a sensor is defined by the signal it generates, expressed in the concentration units of the substance measured[4]. With some sensors the sensitivity rises to a maximum during the device's lifetime. Sensitivity depends on some parameters such as sample matrix, temperature, pressure, and humidity. All these parameters must remain constant during calibration and in the analysis of real samples. Our chemical sensor with the dicarboxylate group has a good sensitivity with different concentrations of samples used.

1.1.3 Lifetime

Many factors affect the lifetime of a sensor. For optical sensors based on membrane-bound recognition, molecules lose their ability to function by leaching-out effects. Photodegradation may occur if the readout device

requires absorption of light such as most types of optically sensitive materials. Photodegradation of chromophores can occur when absorption is used for sensing. This will limit the lifetime of the sensor. Also the photo bleaching effect on optical sensors may reduce the lifetime to less than a year[4].

1.1.4. Response Time

Some manufacturers define it as the time required for a signal to reach about 90% of its final value. While others sometimes prefer the 95% or even 99% level[4]. The response time should be ranged from several seconds to a few minutes, depending on the thickness of the sensing element, and the extent to which the analyte has to be interacted with the sensing element. Response times for chemical sensors are in the range of seconds, but some biosensors require several minutes to reach a final reading, sometimes in environmental control, the time is reasonable; it is in minutes.

The response time for a sensor is generally greater for low analyte concentration than for higher concentration, this is related to the diffusion factor. There are some factors that affect the response time such as the surface roughness of the sensor and the dead volume of the measuring cell.

In the presence of strongly interfering substances, the response time for a chemical sensor might increase as a result of an increase in the time required to reach final equilibrium[4].

1.1.5. Stability

The stability of a chemical sensor is usually subject to a significant aging process. In this process, most sensors lose some of their selectivity, sensitivity, and stability. Some sensors can be rejuvenated, such as the glass pH electrode[4]. Some sensors based on polymer swelling lose their stability due to mechanical stresses associated with swelling and shrinking, and cracking or other forms of mechanical deterioration. The forces that cause the polymer to swell create internal stresses that often cause the polymer to crack. If the polymer is immobilized in a solid substrate, then it is constrained so that it can only swell in the direction perpendicular to the surface. This leads to shear forces at the polymer/substrate interface that can cause delamination[5]. These factors are in minimum if the microspheres polymer dimensions are in the order of few micrometers. By suspending the microspheres in a hydrogel membrane allows them to swell freely in all directions, increasing the volume change due to swelling and circumventing the problem of delamination.

1.1.6. Limit of Detection

The limit of detection (LOD) is defined as three times the standard deviation of the blank value (the lowest measurable level), expressed in concentration units. The definition used when traces of the analyte would be present or might easily be carried out into the calibration process by solvents or reagents. This case is found in extremely sensitive sensors[4].

1.1.7. Reliability

It is defined as the extent to which an experiment, or measuring procedure yields the same results on repeated trials. Analytical results are incomplete without an estimate of their reliability.

1.1.8 low cost

Both the preparation and instrumentation of a sensor should have low cost.
For example, some optical sensors, such as optical sensors based on polymer swelling use low cost LEDs as light source and photodiode as detectors. While conventional methods require sampling as well as sample preparation, and expensive instrument.

1.2 Classifications of chemical sensors

There are four major subclasses of chemical sensors: thermal, mass, electrochemical, and optical; they are based upon the measurement of heat, mass, electronic, and optical quantities, respectively.

1.2.1 Thermal Sensors

These chemical sensors use the heat generated by a specific reaction as the source of analytical information. These sensors represent a form of in situ microcalorimetry, which could be performed in a batch mode. The general strategy is to place the chemically selective layer on top of a thermal probe and measure the heat evolved in the specific chemical reaction taking place in that layer, as the change in temperature of the sensing element. Thermal sensors constitute the smallest class of sensors. Thermistors and pyroelectric devices are two thermal probes used for monitoring thermal processes[1].

1.2.2 Mass Sensors

Microbalances and microgravimetry can be regarded as mass sensors. Piezoelectric crystals have been used as microbalances due to their small size, high sensitivity, and stability. They are relatively inexpensive, and readily available. α-Quartz is the material selected for the most piezoelectric sensor applications, because it is inexpensive and has a relatively high piezoelectric coefficient. The sensor operates by applying a voltage -created by an applied pressure- to the crystal, which causes it to propagate a wave across the crystal at a certain frequency. Since the chemical sensing layer which interacts with the analyte of interest is applied to the top of the crystal. The interaction between the sensing layer and the chemical causes an increase in the mass crystal. The addition of mass to the crystal changes the frequency of the propagating wave, which can be easily measured[1].

The major advantages of mass sensors are their simplicity of construction and operation, their light weight, and the low power required. They also have high sensitivity and can be used for a very broad range of compounds[1].

1.2.3 Electrochemical Sensors

Electrochemical sensors are the largest and oldest group of chemical sensors. They are divided by their mode of measurement into potentiometric, amperometric, and conductimetric sensors. There are some common rules, which apply to all electrochemical sensors, the cardinal one being the requirement of a closed electrical circuit that is at least two electrodes constitute an electrochemical cell. From an electrical point of view, the two electrodes can be a sensor electrode and a signal return[1].

Electrochemical sensors have certain advantages. Measurements can be made on exceedingly small volumes of sample with miniaturized electrodes. Also the signal from electrochemical cell is electrical. So, no conversion to an electrical signal for the measurement process is required. Electrochemical cells exhibit certain disadvantages, which have restricted their implementation as sensors. The main one is their inherent lack of selectivity in comparison with electrical techniques. A second disadvantage is the necessity of the references electrode in order to maintain constant half cell potential[2].

1.2.4 Optical Chemical Sensors

Fiber optic chemical sensors (FOCS) are based upon the interaction of electromagnetic radiation passed through fiber with matter presented at one end of the fiber optic chemical sensor. Optical fibers and waveguides can transmit light over large distances and with minimal loss of intensity. This makes optical sensors particularly attractive for remote sensing and for applications where the use of electricity may be hazardous[1]. FOCS has essentially three major components: light source, optical fiber, and a photodetector[6-8]. The advent of optical fibers has initiated a revolution in telecommunications technology and is producing a subsequent and possibly equal impact on chemical sensor technology[2].

Since optical fibers can be many meters in length, are flexible, and have diameters typically 125-1000μm, it is feasible to perform continuous spectroscopy in inaccessible or remote sites. Sensors based on fiber optic technology provide some interesting advantages over other sensors. Their sturdy and simple construction permits placement in harsh environments[2]. They are immune to electromagnetic interference, and require no reference electrode, and no electrical shocks happen[2,9]. Also their low cost permits the sensors to be useful for many applications[2]. There is a great degree of selectivity inherent in the transduction part of optical sensors given by the choice of wavelengths, polarization, etc[1].

Fiber optic sensors are classified as intrinsic or extrinsic sensors[2]. With an intrinsic sensor the optical fiber itself acts as an optical component and is modulated directly by the change in a physical parameter, thus altering the transmitted light. Intrinsic sensors exist for the measurement of temperature, magnetic field, acoustics, strain and electrical current as well as other physical parameters. These sensors use the fiber as the chemically sensitive component. They use developed fibers in which, the core, cladding or jacket materials are used as the transduction element. Essentially, a physical property of the analyte can be measured directly through the fiber with or without a specific chemical sensing element. An example of this type of sensor is the evanescent wave sensor. Extrinsic sensor is used for specific chemical detection and requires the association of an optical transducer with the fiber. The transducer must induce an optical signal change in response to the selective detection of an analyte in a complex mixture. The transduction of chemical information usually takes place outside of the fiber. A chemical recognition element is attached to the tip of the fiber, and fluorescence or absorbance measurement is monitored.

FOCS have a variety of applications in different areas, such as water analysis, biological and medical research, industrial bio processes corrosion

and combustion. Several papers on gas, vapor, and humidity sensors have been produced[12]. Gas sensors such as hydrogen[13], methane and related hydrocarbons[14], oxygen[15], NO gas[16], and CO_2 gas sensor[17,18]. Humidity sensors have been described that are based on highly different schemes[19]. Numerous fiber ion sensors for all kinds of inorganic ion including the proton (pH), and salinity have been reported. Also sensors for organic compounds such as pollutants, agrochemicals, explosives, drugs and pharmaceuticals have been developed. In biosensors, a biological component is used in the recognition process[12]. Typical components include enzymes[20], antibodies, oligonucleotides, and whole cells[21].

1.3 Types of Optical Sensors

1.3.1 Optical Sensors Based on Indicator

There has been an interest in chemical sensors consisting of immobilized indicators coupled to a spectrometer through fiber optics. It is necessary to add reagents that interact with the analyte to form a product, which is optically detectable. There should be a convenient method for formulating the polymeric indicator substrate and coupling into fiber optics. Different methods for immobilizing indicators and coupling them to optical fibers

have been employed. Although these methods offer advantages and disadvantages, none of them combines convenience with the ability to reproducibly control both the amount of indicator and the amount of immobilization substrate. A method for immobilizing indicator for fiber optic sensing has been reported[22]. Cyanuric chloride is used to couple indicator to poly (vinyl alcohol) (PVA), which, is then cross-linked with glutaraldehyde in the presence of acid, which acts as a catalyst. Further work describes the response characteristics of sensors for pH and Mg^{2+} prepared using PVA as the indicator substrates[2]. This kind of sensor has some limitations, such as indicator instability, because of leaching and photodegradation.

1.3.2 Optical Sensors based on polymer swelling

Sensors based on polymer swelling include chemical functional group as the chemically selective, and sensitive layer. This type of chemical sensor has been investigated several years ago. In 1990, the first fiber optic chemical sensor based on polymer swelling was developed using ion exchange materials of sulfonated polystyrene and sulfonated dextran to detect changes in the ionic strength of aqueous solution. Interaction between the analyte and the functionalized polymer caused the bead to shrink[23]. This polymer bead

was coupled to optical displacement within the optrode. The change in the size of the polymer force a flexible diaphragm causing it to move to detect the amount of light reflected into an optical fiber. The commercial ion exchange materials that were used in the sensor limited their ability to swell and shrink due to the high crosslinking levels of these materials causing the beads to crack during successive shrinking and swelling cycles. As a result the lifetime of the sensor was short, using these types of polymers.

Mechanically robust amine derivatized polystyrene for pH sensing based on polymer swelling was prepared in 1993[25]. The beads that change size as a function of pH have been prepared by suspension polymerization. Poly (Vinyl benzyl chloride) was cross-linked with divinyl benzene in the presence of toluene and Kraton G1652 and was followed by reaction with pure diethanolamine. Kraton G1652, the styrene-ethylene/ butylene- styrene copolymer, as a toughening agent that improves the mechanical properties of the polymer beads. As the pH decreases, a charge on the amine group produced by protonation, causing the polymer to swell due to electrostatic repulsion between charged sites on the polymer. The polymer beads undergo many swelling and shrinking cycles without degrading mechanically but they are softer than desired for use in a pH sensor based on polymer swelling[25]. Later work was done at low crosslinking levels to provide a

large response and long lifetime sensor[26]. But using polymer beads was avoided since the low crosslinking levels are too soft producing a force, which is not enough to move reflected diaphragm.

Further work proved that polymers with added Kraton G1652 were good diffuse reflectors[27]. The optical system included an LED as the light source, a photodiode detector and a fiber optic coupler as a beam splitter. Electrostatic repulsion between protonated amine groups caused the polymer to swell when exposed to acidic medium. Intensity decreased as the pH is lowered from 8.0 to 6.5 with response time of several minutes. But this sensor has limitations. Crack formation due to swelling and shrinking induced stresses during the first few cycles. The response time; swelling of sensor in acid was complete after 3 minutes, while shrinking in base takes longer time. Also the mechanical stability decreased after successive shrinking and swelling cycles.

Polymer substrates for optical sensors were produced in 1994[27]. Bulk free radical polymerization was used to prepare membranes for chemical sensing based on changes in light reflectance from amine modified, rubber toughened poly (VBC-co-divinylbenzene). When the polymer swelled, the membrane was clear and reflected less light, while when the polymer was

unswollen; the cross-linked membranes were turbid and scattered light. Swelling decreased the refractive index of the hydrated polymer and brought it closer to the refractive index of water. A limitation in this design was that as the polymer swelled, it did so to the point it would delaminate from the substrate to which it was attached. To control this problem, the use of the polymer microparticles embedded in a hydrogel was examined. Derivatized VBC particles were suspended in a hydrogel membrane to become scattering centers; therefore the hydrogel served as a medium to suspend the particles.

There are many advantages of this design. The polymer can swell in all directions resulting in a larger optical signal due to larger change in volume[28]. Another advantage is that it is easy to attach the hydrogel membrane to fiber optic materials. The hydrogel membrane does not form an interaction with the microspheres. It only provides a medium for the microspheres to be suspended in. By suspending the microspheres in a membrane allowing them to swell freely in all directions, increasing the volume change due to swelling and circumventing the problem of delamination.

Derivatized lightly cross-linked polymer microspheres that swell and shrink as a function of analyte concentration for chemical transduction are prepared

by dispersion polymerization. The microspheres of diethanolamine derivatized polystyrene are dispersed into a polyvinyl alcohol hydrogel membrane. Swelling causes the microspheres refractive index to be closer to the hydrogel refractive index resulting in a decrease in membrane turbidity. This can be measured as either a change in transmitted or reflected intensity. The advantage of this approach is that it can be applied at any wavelength including near-infrared that are used for fiber optic telecommunications[5].

Swellable polymer substrates in different sensing schemes, including magnetochemical sensor and optical chemical sensor were used[29]. Lightly cross-linked, aminated polymers that swell and shrink were prepared. The polymer swelled at low pH causing a change in the magnetic or optical property. Poly (vinyl benzyl chloride-co-2,4,5- trichloro phenyl acrylate)(Poly (VBC/TCPA)) microspheres were prepared by dispersion polymerization. (VBC/TCPA) microspheres were used in several optical sensing methods. Thus poly vinyl alcohol membranes with (VBC/TCPA) microspheres were used to examine the feasibility of monitoring solution pH by surface plasma resonance. The pH sensitive hydrogel membranes were incorporated into two types of magnetochemical sensors; the magnetostatic coupled sensor and the magneto elastic sensor. Both sensor designs responded to solution pH due to swelling and shrinking of the hydrogel.

Two advantages of (VBC) microspheres in a poly (hydroxyethylmethacrylate) “poly HEMA” membrane were detected. The first is that no change in response was observed after 100 swelling and shrinking cycles. This confirmed the reproducibility of the response. The second advantage was when the membrane was exposed to 80^{o}C or light for 40 days; a small change on the magnitude of the response was observed.

There are many advantages of using microspheres suspended in a hydrogel membrane; the mechanical stability of the sensor surface, the mechanical stability after many shrinking and swelling cycles, and shorter response time. Derivatized lightly cross-linked polymer microspheres that swell and shrink as a function of pH have been investigated[30]. The microspheres were immobilized in hydrogels forming a sensing membrane. As the microspheres swell as a function of pH, the turbidity of the membrane decreases due to the small difference between the refractive index of the hydrogel and the microspheres. While when the difference is large, the membranes look turbid. The change in turbidity of the membrane was monitored by UV-vis-NIR spectrophotometer[30].

The phenomenon of polymer swelling for optical sensing without the mechanical problems inherent in bulk polymer swelling was exploited in 1999. The new type of membrane can be coupled to optical measurement in the near infrared, including remote measurements through optical fibers[31]. The membrane has been prepared by suspending aminated polystyrene microspheres in a hydrogel. The swellable polymer, aminated polystyrene, is formulated in the form of microspheres with diameters less than 1μm. This minimizes the internal stresses that accompany swelling.

There is an interest of detection of heavy metals. Human activities have modified and interfered with natural cycles and caused a release to the aquatic and terrestrial systems of heavy metals[24]. Some heavy metal ions are essential for many organisms but in small doses, where high doses may affect the ecosystem and human health, Especially in the case of very toxic metals even in small doses. Heavy metals are metals with a density larger than $5gm/cm^3$.

A magneto-acoustic sensor was used to monitor viscosity in starch solution, water loading and 2-hydroxyethyl methacrylate polymerization. Poly (vinyl benzyl chloride) microspheres were prepared by suspension polymerization and then derivatized to introduce dicarboxylate groups onto the polymer

backbone. Poly (vinyl benzyl chloride-trichlorophenyl acrylate) microspheres were prepared by dispersion polymerization and then derivatized to introduce amine groups onto the polymer backbone. The derivatized polymer microspheres swell and shrink with changing pH. They were entrapped in a hydrogel membrane and the membrane turbidity was investigated by UV/vis spectrophotometry. Membrane turbidity increased with pH from 6.0 to 8.0 for entrapped aminated poly (VBC-TCPA) microspheres, and decreased with pH from 2.0 to 8.0 for entrapped dicarboxylated poly VBC microspheres[32].

Chelating resins have been employed successfully in some areas such as removal of harmful trace metal ions, because of the highly selective adsorptivity for heavy metal ions. Polymers containing carboxylic acid groups showed adsorptivity for alkali-metal ions such as Na^+ and K^+, and alkaline-earth metal ions such as Mg^{2+} and Ca^{2+} as well as for nickel and zinc[33].

Our research focused on developing an optical chemical sensor based on swellable dicarboxylate functionalized polymer microspheres. There are three main goals of this work. The first goal is to develop a sensor for sensing divalent metal ions. The second goal is to apply this sensor to

response to certain pH ranges. Also, in this work, the sensor was evaluated in respect to chemical and mechanical stability, including temperature effect, sensitivity, response time, reproducibility, and its lifetime.

CHAPTER 2

EXPERIMENTAL

2.1 Reagents

Diethyl malonate, glutaraldehyde, N, N-Dimethyl formamide, these chemical reagents were obtained from sigma Aldrich Company. Sodium hydride, hydrochloric acid, ammonia buffer, ethylenediaminetetraacetic acid (EDTA), methanol, sodium perchlorate, sodium chloride, potassium chloride, calcium chloride, magnesium chloride, nickel chloride ($NiCl_2.6H_2O$), cadmium chloride ($CdCl_2.H_2O$), zinc chloride, lead acetate (Pb $(CH_3COO)_2$. $3H_2O$). All chemicals were of analytical grade reagents.

All Polyvinyl benzyl chloride crosslinked with divinyl benzene (2% mole) was supplied by professor W. R. Seitz's group at the University of New Hampshire, USA. All solutions were prepared in deionized distilled water. Brintton-Robinson buffer solutions were prepared at 0.1M buffer concentrations and 0.1 ionic strength adjusted by 1 M of sodium perchlorate.

2.2 Apparatus

A Perkin-Elmer Lambda 5 UV-visible spectrophotometer was used to carry out all the spectrophotometric measurements. Most spectrophotometric measurements were performed at room temperature (25^{o}C), while the study of effect of temperature was done at higher temperatures. A pH meter was used during the preparation of buffer solutions of different pH values.

2.3 Procedures

2.3.1 Synthesis of Polymer with Diethyl Malonate Groups

Diethyl malonate was reacted with chloromethylated polystyrene cross-linked with divinylbenzene. Thus, a solution of diethyl malonate (5.6 g) in 30mL of N,N-dimethylformamide (DMF) was added dropwise to 50mL of DMF in which sodium hydride (1.0 g) was suspended. The dried polymer microspheres (2.0 g) were added to the solution and stirred for four days at 80^{o}C. The resulting product was filtered and washed successively with ice-cold distilled water, then with hot distilled water at 70^{o}C and finally with

methanol. The derivatized polymer was dried at 40^{o}C in a vacuum oven for a few hours, then at room temperature for 3 days and then weighed.

2.3.2 Hydrolysis of the Diethyl Malonate Group

Diethyl malonate polymer (2 g) was placed in 100mL of a 6M sodium hydroxide solution. The mixture was stirred for three days at 100^{o}C under reflux. The product was washed many times with distilled water followed by drying at 50^{o}C overnight.

2.3.3 Determination of the Polymer Capacity

The amount of the dicarboxylate groups on the polymer was determined by acid-base titration. In addition, the polymer capacity for metal ion was determined by pretreatment with 1.0M Ca^{2+} solution, then by washing extensively with distilled water. The adsorbed metal ions on the polymer were eluted by 1.0M HCl. Then, the eluted Ca^{2+} ions were determined by titration with standard EDTA solution, after the pH had been adjusted by ammonia buffer of pH 10.0[34].

2.3.4 Preparation of the Sensing Element

In order to prepare 1% of polymer microspheres dispersed in a hydrogel membrane as a sensing element, 30mg of the derivatized microspheres were soaked in a few drops of DMF for a few minutes. Then, 3.0ml of polyvinyl alcohol aqueous solution (2.5%) was added and stirred until the polymer microspheres were dispersed and the mixture became uniform. A solution of 100 μl of 8% glutaraldehyde was added to the mixture and stirred for a few seconds. This was followed by addition of 100 μl of 3.0M HCl solution under continuous mixing. A few drops of the resulting solution were immediately transferred and spread over the clear side of a plastic cuvette. The sensing membrane was allowed to formulate and stick in position. The resulting sensing membrane was washed with distilled water and stored in either distilled water or basic buffer.

2.3.5 Preparation of Stock Brinton Robinson Buffer Solution

This buffer was prepared by adding acetic acid (2.3 ml), and phosphoric acid (2.7 ml) to a solution of boric acid (2.5 g) in distilled water, and the volume of the solution was bought up to one liter by adding distilled water.

2.3.6 Preparation of buffer solutions with different pH values.

Different pH solutions were prepared using Brinton Robinson buffer. To adjust the pH, 1.0M sodium hydroxide was added to 250 ml of Brinton Robinson buffer until the required pH was reached. This was determined by a pH meter. The pH solutions, which were prepared, ranged from pH 4.0 to pH 10.5. The ionic strength of all pH solutions was adjusted by adding 1.0 M sodium perchlorate. Then, the total volume of each pH solution was adjusted to 350 ml by the addition of distilled water, and then the final pH value was measured.

2.3.7 Preparation of metal solutions

To prepare different concentrations of different metal ions, the solution of metal ion was prepared by dissolving the metal in distilled water to obtain certain concentration, and then dilution was made on this concentration to obtain higher concentrations of the same metal ion. Different concentrations of Ca^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+}, were changed from 0.0001M up to 0.01M, for Mg^{2+}, concentrations were changed from 0.01M up to 0.5M, and for Pb^{2+}, from 0.0001M up to 0.05M.

2.3.8 Optical Measurements

The cuvette with the sensing element stuck on its sidewall was secured in the cell holder of a Perkin Elmer conventional spectrophotometer such that the sensing element membrane was positioned in the light beam path. The change in optical properties due to swelling and shrinking of microspheres is measured as absorbance as shown in figure 2.1. The solution in the cuvette was changed by using a disposable pipette. The change in turbidity of the sensing element as a function of analyte concentration was measured as absorbance. The spectrum was obtained at different periods of time until it reached a steady state.

To measure the absorbance as a function of pH, Brinton-Robinson buffer with an ionic strength of 0.10 M was used. Reproducibility of the sensing element was tested by cycling the sensing element between pH 7.0 and pH 9.0. The cell containing the sensing element was filled with a buffer solution of pH 7.0, the absorbance was measured, then the solution was replaced by a solution of pH 9.0, and the absorbance was measured. The trial was repeated four times.

To measure the response time to pH, buffer solution was changed from pH 9.0 to pH 3.0 from the cell of the sensing element. Run was taken each 3 minutes along 30 minutes, and the absorbance was measured each run. To

change the pH from 3.0 to 9.0, the buffer solution of pH 3.0 filled into the cell of the sensing element was replaced by a solution of pH 9.0. Run was taken each 3 minutes, and the absorbance was measured each run.

To measure the response to variation in pH, the buffer solution was changed from pH 4.0 to higher pH as required until reach pH 10.5. Buffer solution of pH 4.0 was put into the cell containing the sensing element, the absorbance was measured, then the solution was replaced by a solution of pH 4.5, the absorbance was measured, and so on with higher pH solutions until reached a solution of pH 10.5.

To investigate the response of the sensing element to metal ions at different concentrations, the solution containing the metal ion was filled into the cell of the sensing element starting with the lowest concentration. Then after the absorbance was measured, the solution was replaced by a solution containing higher concentration of the same metal ion, and so on with higher concentrations.

Response times for Zn^{2+}, Cd^{2+}, and Ni^{2+} metal ions were measured. The solution of the metal ion with concentration of 0.005 M was filled into the

cell of the sensing element; the absorbance was measured each minute along 30 minutes.

2.3.9 Measurement of response at different temperatures

To test the effect of temperature on the sensor, the cell of the sensing element was filled with 2 X 10^{-4}M Ni^{2+} at pH 6.11, then the absorbance was measured at 25^{o}C, 30^{o}C, 35^{o}C, and 40^{o}C, by connecting the UV-visible Spectrophotometer cell with a thermostat medium, starting at room temperature, and then raising the temperature to the required value.

2.3.10 Regeneration of The Sensing Element

In order to elute the metal ion from the sensing element after measuring the response time to each metal ion, the sensing element was regenerated by 1.0M HCl, then by reconditioning in a basic buffer. After using the sensor, it was stored in a basic buffer solution, in order to avoid dryness of hydrogel membrane.

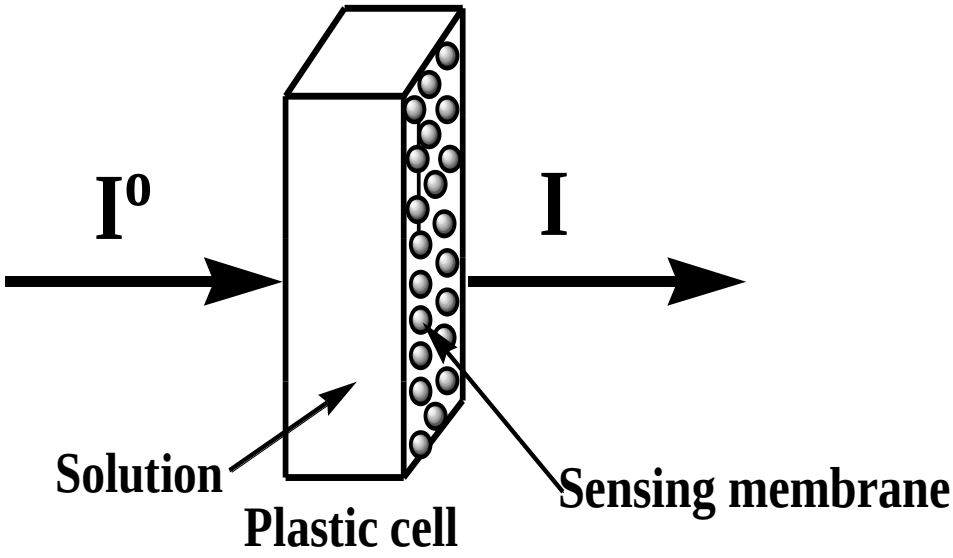


Figure 2.1: Diagram of optical system.

CHAPTER 3

RESULTS AND DISCUSSION

This study investigates the variation in absorbance with pH of our polymer microspheres since it is pH-sensitive polymer. Also it shows the response to some divalent metal ions. The effect of temperature on the sensor response was also studied.

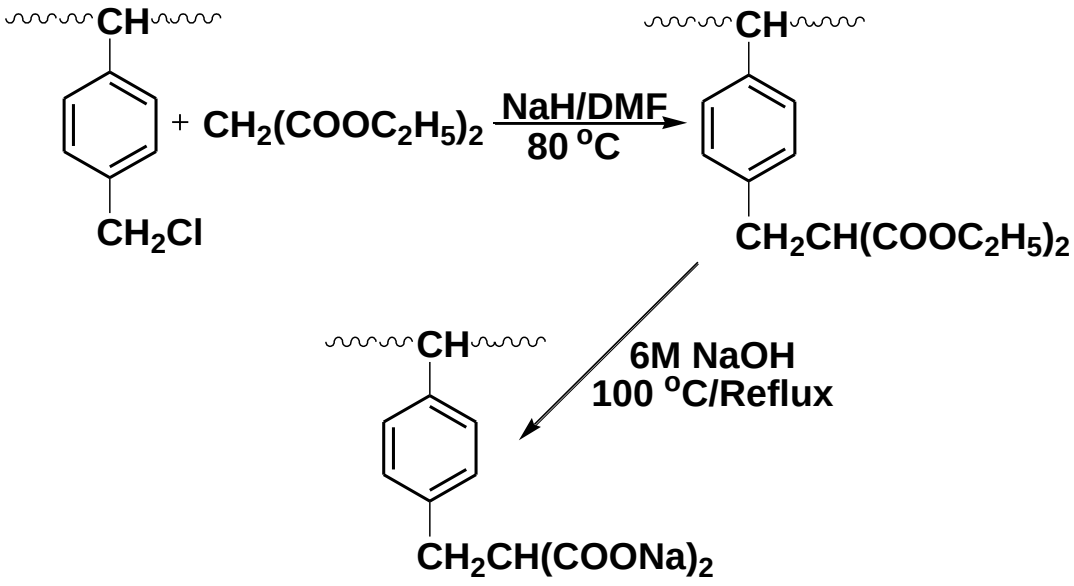
The polymer microspheres containing a diethyl malonate group, which was prepared by the reaction of polyvinyl benzyl chloride with diethyl malonate, and then hydrolyzed in sodium hydroxide solution as indicated in scheme 3-1.

The project is based on changes in the optical properties of the sensing element that accompany shrinking and swelling. In this pH sensitive polymer, as the carboxylic acid on the polymer deprotonated in basic medium, the repulsion occurs between adjacent negative charges resulting in swelling of the polymer, while when the dicarboxylate groups are neutralized by protons, the polymer microspheres shrink. Also, when the deprotonated carboxylic groups on the polymer bind with metal ions, their negative charges are neutralized and the polymer microspheres shrink as indicated in figure 3.1. A change in the optical properties of the sensing

element occurs as a result of swelling and shrinking of the polymer microspheres. This change in optical properties is related to the change in the difference in the refractive index between microspheres and that of the hydrogel membrane.

3.1 Polymer Capacity

The determination of pH, copper and calcium ions using the swellable dicarboxylate functionalized polymer microspheres was carried out. Acid-base titration indicated that the amount of carboxylic groups was 2.773 mmole per gram of polymer. While the content of carboxylic groups was calculated to be 2.238 mmole per gram of polymer. Titration with EDTA showed that the capacity of the derivatized polymer for calcium ions is 1.29 mmole per gram of polymer that is approximately equivalent to half of the content of carboxylic groups, suggesting the formation of 1 to 2 ratio complexes[34].



Scheme 3-1: Synthesis of dicarboxylated polymer microspheres.

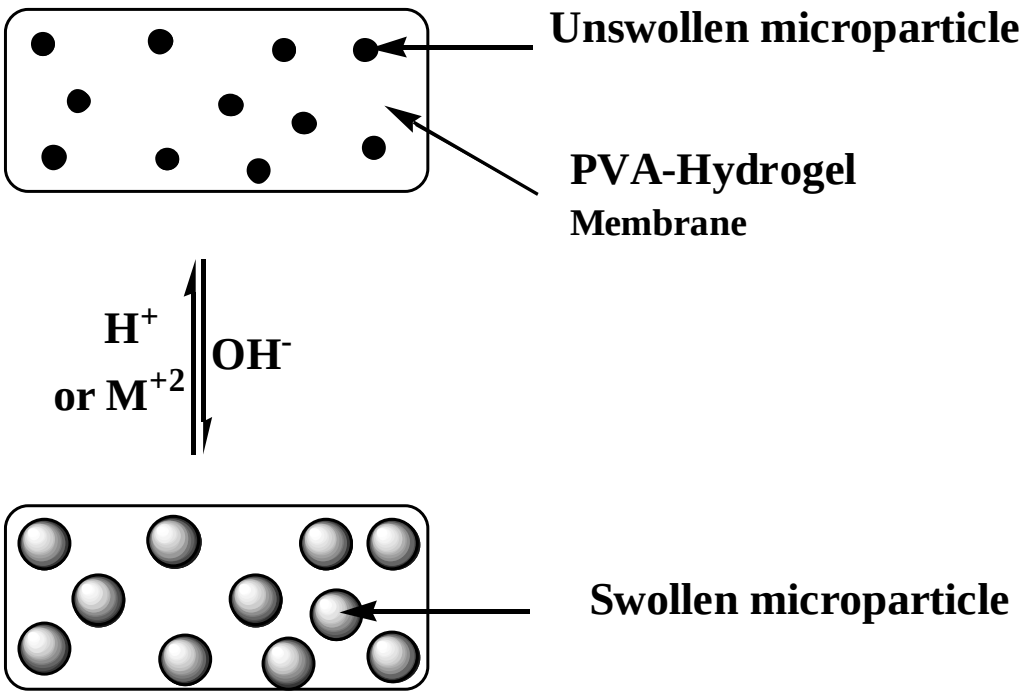


Figure 3.1: Schematic diagram of sensing response to pH and metal.

3.2 Response to pH

When the pH is changed from 3.0 to 9.0, the absorbance decreases with time as a result of polymer swelling in basic solution where the carboxylic groups are deprotonated. On the other hand, when pH is changed from 9.0 to 3.0, absorbance increases with time as a result of polymer shrinking (Fig. 3.2). This is due to protonation of the carboxylic groups. Shrinking in acidic medium takes slightly longer time than swelling in basic medium. Thus, swelling occurs faster than shrinking because swelling begins from the outside of the microspheres, triggering the solution to diffuse into the polymer. Also, shrinking begins from the outside of the polymer microspheres, retarding diffusion of both hydrogen ions into the polymer and water out of the polymer, resulting in a relatively slower response time.

There was no significant difference in the absorption spectra as the sensing polymer was cycled between pH 3.0 and pH 9.0 or between pH 9.0 and pH 3.0. The response time for the pH change from 3.0 to 9.0 is about 3 minutes. While when the pH is changed from 9.0 to 3.0, it takes a longer time about four minutes.

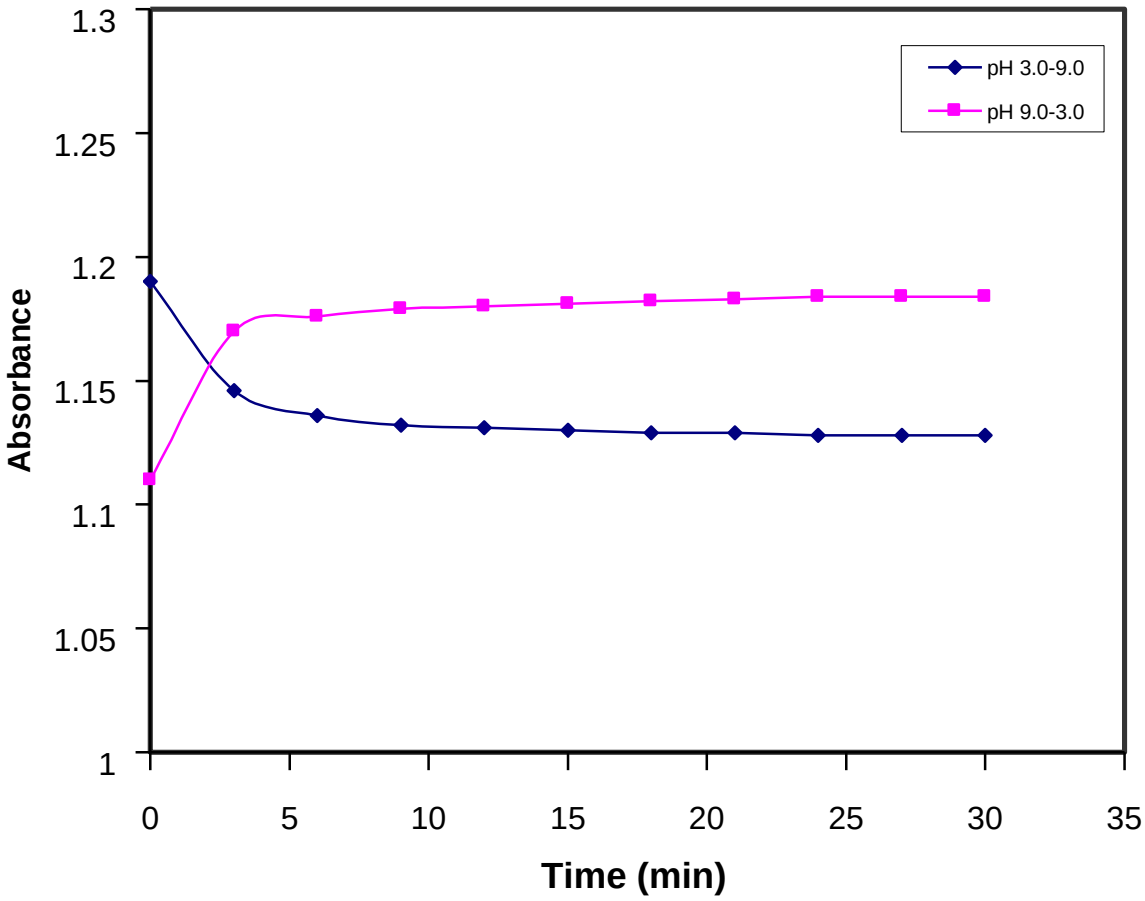


Figure 3.2: Absorbance vs. time for swelling and shrinking.

When the sensing element was cycled between pH 7.0 and pH 9.0, the absorbance value stayed constant (1.11 and 1.09) respectively, as given in Table 3.1 that is an indication of reproducibility of the sensing element.

Table 3-1: Reproducibility results

Trial No.	Absorbance at pH = 7	Absorbance at pH = 9
1	1.11	1.09
2	1.11	1.09
3	1.11	1.09
4	1.11	1.09

The variation in absorbance with pH at wavelength of 800nm is shown in figure 3.3. The measured absorbance is related to the change in turbidity of the sensing element with changing pH. As the pH decreased, the absorbance increased until it reached its maximum value at pH 6.5, where the dicarboxylate groups on the polymer microspheres are protonated leading to shrinking state. Above pH 6.5, the absorbance started to decrease until it reached pH 9.0 where the absorbance reached almost constant value. At pH 9.0, all the dicarboxylate groups on the polymer microspheres are deprotonated and so the polymer microspheres reached their maximum

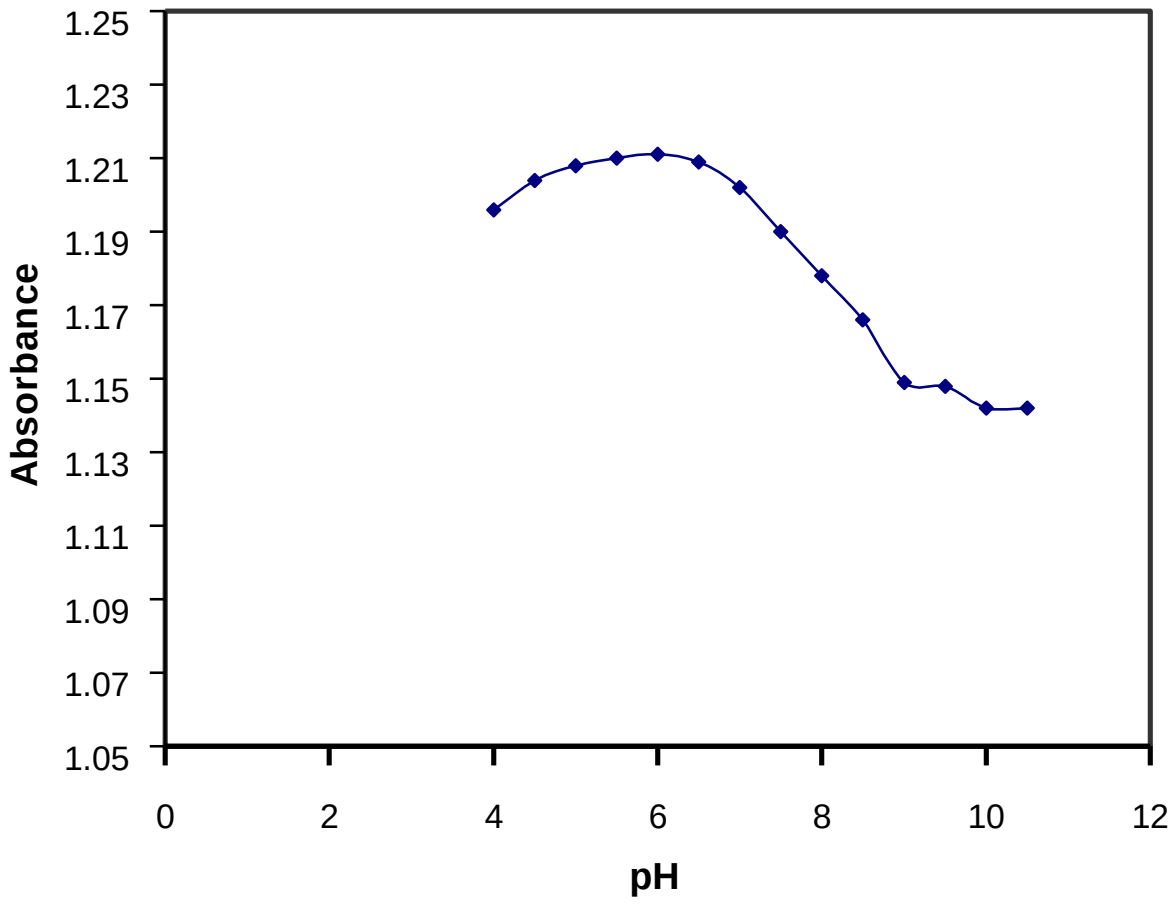


Figure 3.3: Turbidity absorbance vs. pH.

swelling state due to electrostatic repulsion between adjacent negative charges.

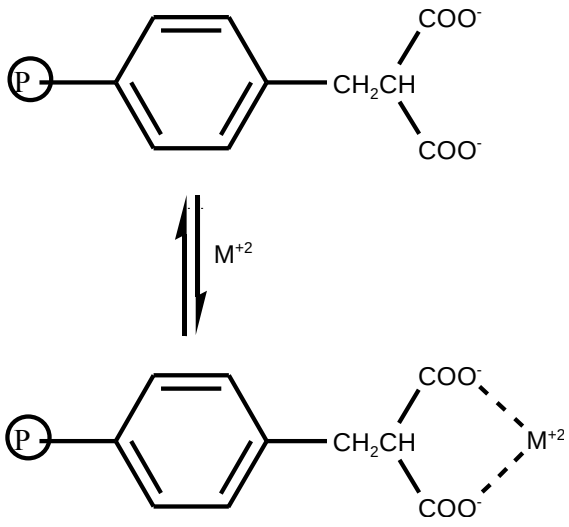
It has an advantage that the microspheres swell between pH 6.5 and 8.5, providing a range that is suitable for many applications.

3.3 Response to divalent heavy metal ions

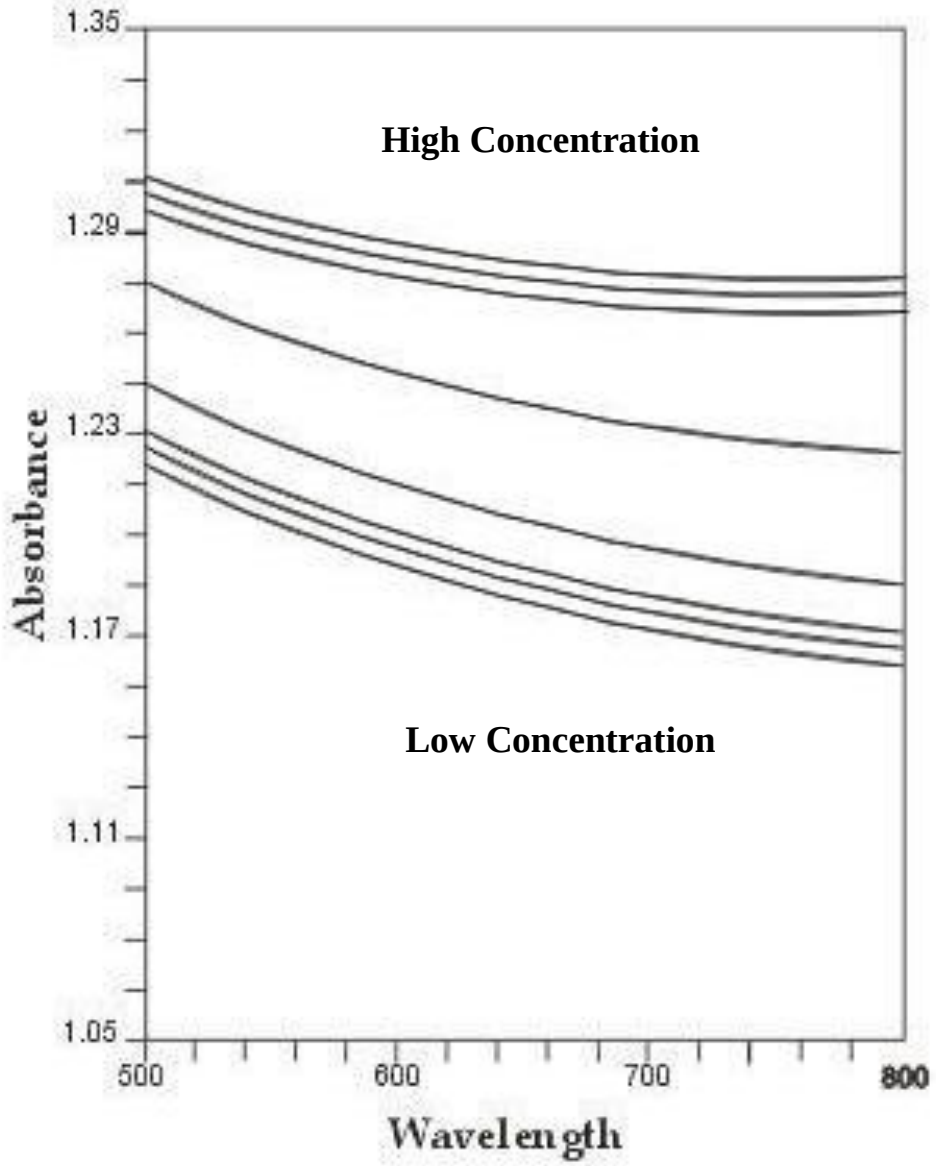
When the dicarboxylate groups are being deprotonated, repulsion occurs between the negative charges on the carboxylate groups resulting in swelling of the microspheres. As the deprotonated dicarboxylate groups bind with the divalent metal ions forming a complex. Due to this binding, the negative charges of the deprotonated dicarboxylic groups are neutralized leading to shrinking of the derivatized microspheres as indicated in scheme 3-2.

The measured absorbance vs. wavelength at different Zn^{2+}, Cd^{2+}, and Pb^{2+} concentrations is shown in plot 1, 2, and 3 respectively. It is obvious from the plots that the range in the absorption spectra between two concentrations is approximately constant especially at low concentrations. As shown in figure 3.4, the absorbance increased with increasing Zn^{2+} concentration as a result of complex formation between ions and the deprotonated

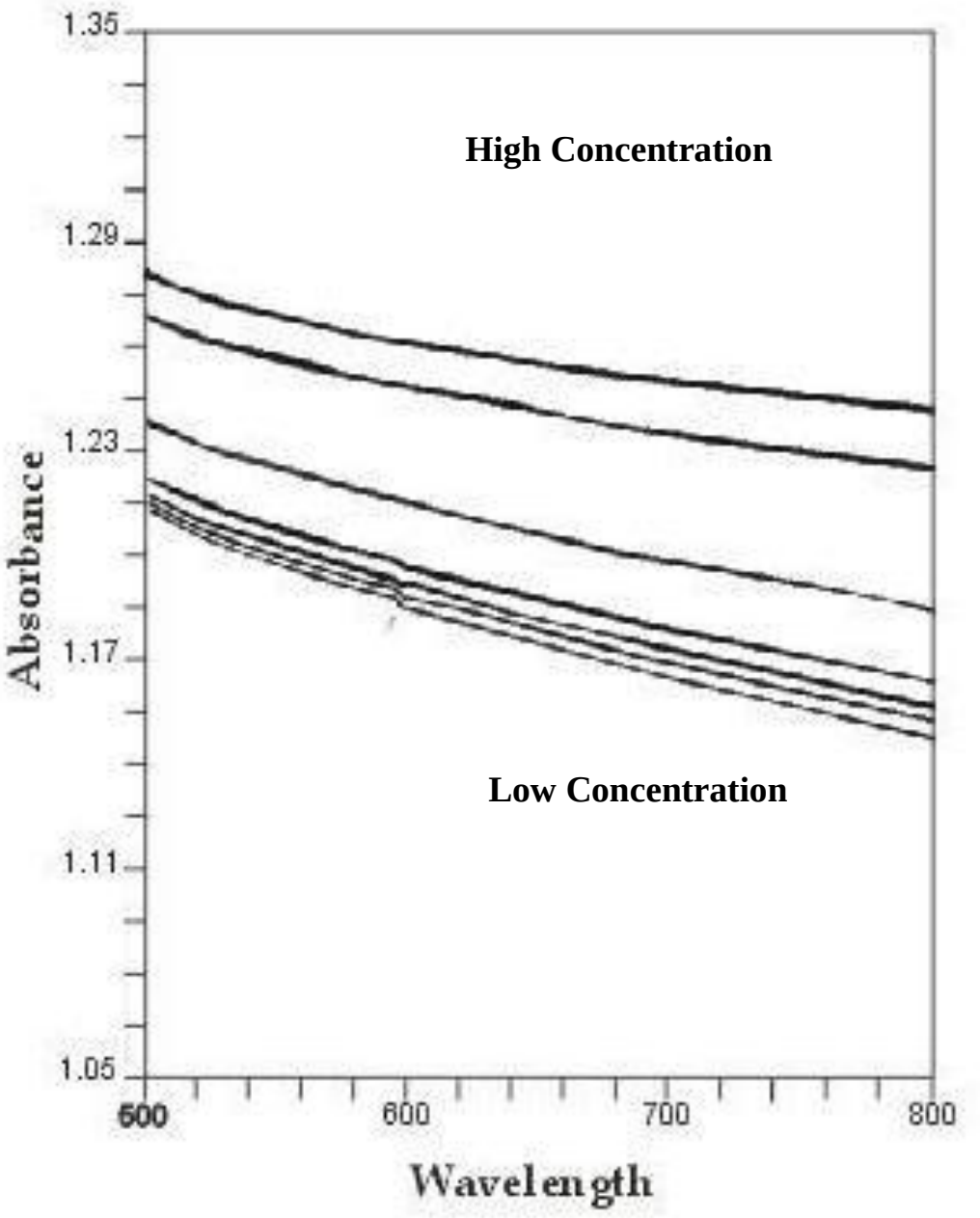
dicarboxylate group, causing the polymer microspheres to shrink, and so absorbance increases. At concentration of 1 x 10^{-4}M and up to 5x10^{-3}M, an increase in absorbance was observed.



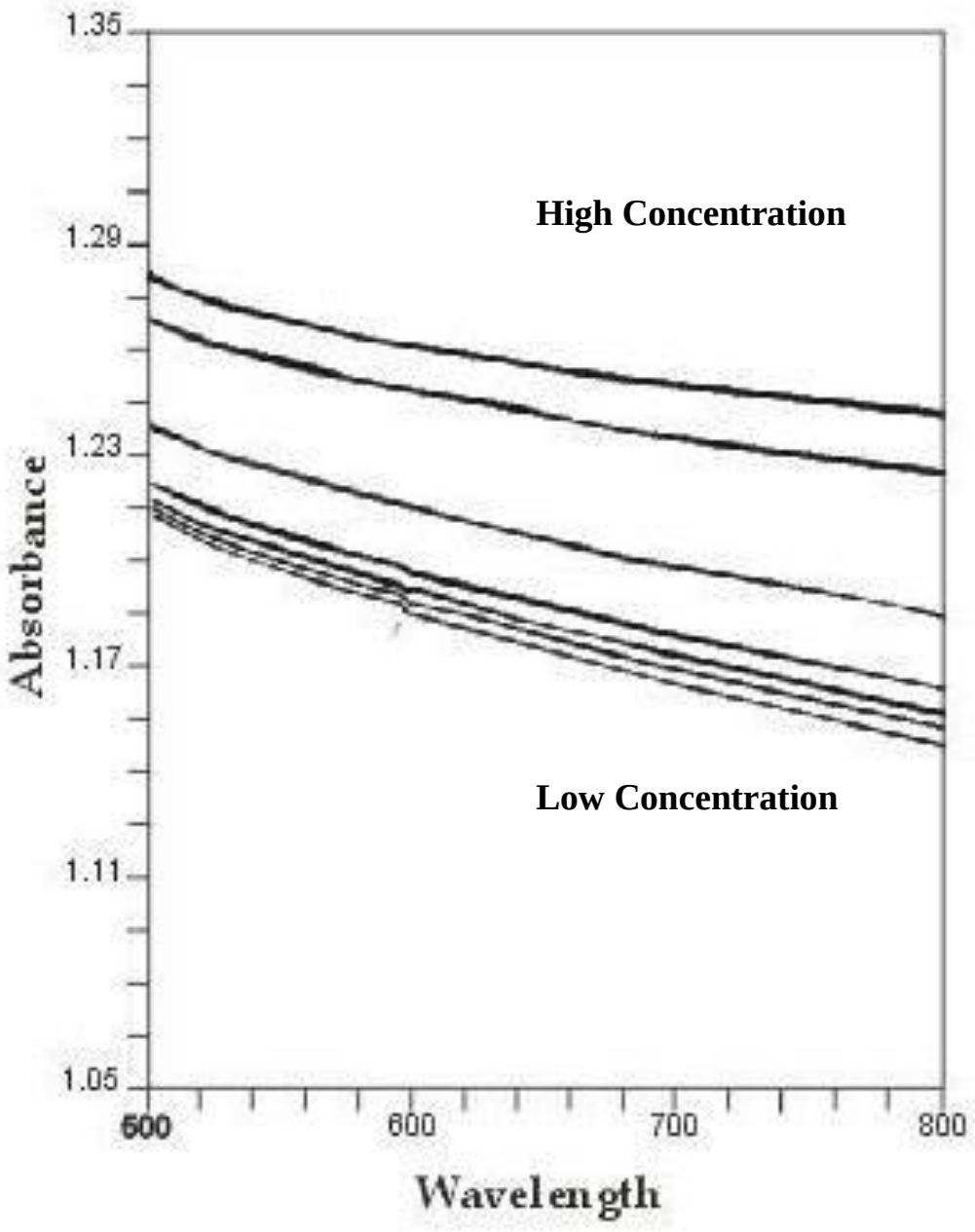
Scheme 3-2: complex formation with divalent metals. (PE= Polyethene)



Plot 1: Variation of absorbance vs. wavelength of different Zn^{2+} concentrations.



Plot 2: Variation of absorbance vs. wavelength of different Cd^{2+} concentrations.



Plot 3: Variation of absorbance vs. wavelength of different Pb^{2+} concentrations.

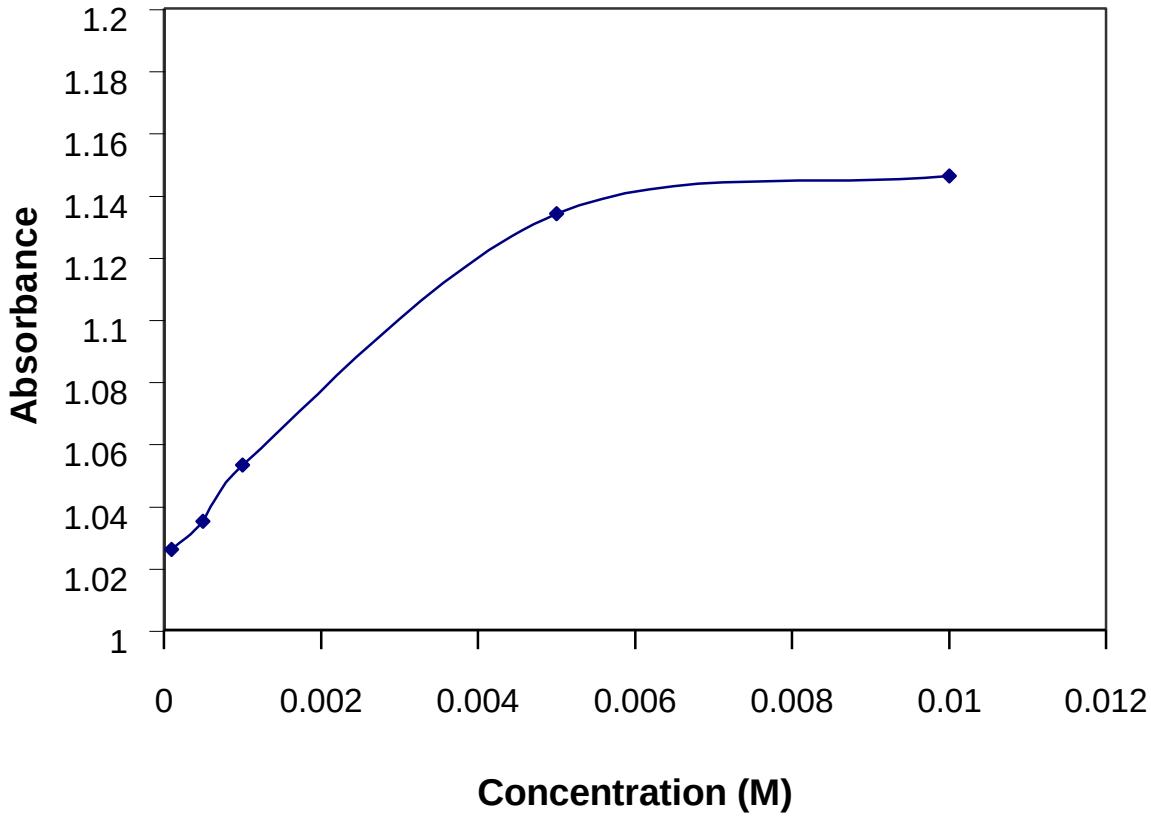


Figure 3.4: Turbidity absorbance vs. concentration of Zn^{2+}.

Similar response to Ni^{2+}, Cd^{2+} and Pb^{2+} was observed. The variation in absorbance with Ni^{2+}, Cd^{2+} and Pb^{2+} concentrations measured at wavelength of 800nm is shown in figures 3.5, 3.6 and 3.7 respectively. There is an increase in absorbance with increasing concentration for all of the mentioned metals. For Ni^{2+} and Cd^{2+}, the absorbance increased when concentration is raised from 1×10^{-4}M to 5×10^{-3} M. while for Pb^{2+}, the absorbance increases with a higher concentration. There is an increase in absorbance as the metal ion concentration increases. The response to metal ions is up to $5x10^{-3}$M to all of Zn^{2+}, Ni^{2+}, and Cd^{2+}, but it is up to $5x10^{-2}$M for Pb^{2+}.

Figure 3.8 compares the variation in absorbance with time for three metal ions: Ni^{2+}, Zn^{2+}, and Cd^{2+} of 0.005M. When the sensing element is exposed to 0.005M of one of the above metal ions solution, the absorbance increased as a result of microspheres shrinking, then it reached a constant value. This increase in absorbance is a result of the formation of the complex between the metal and the dicarboxylate group. As seen in figure 3.8, the response time to Zn^{2+} (16 minutes) is longer than that to Cd^{2+} (12 minutes) which the is longer than that to Ni^{2+} (10 minutes).

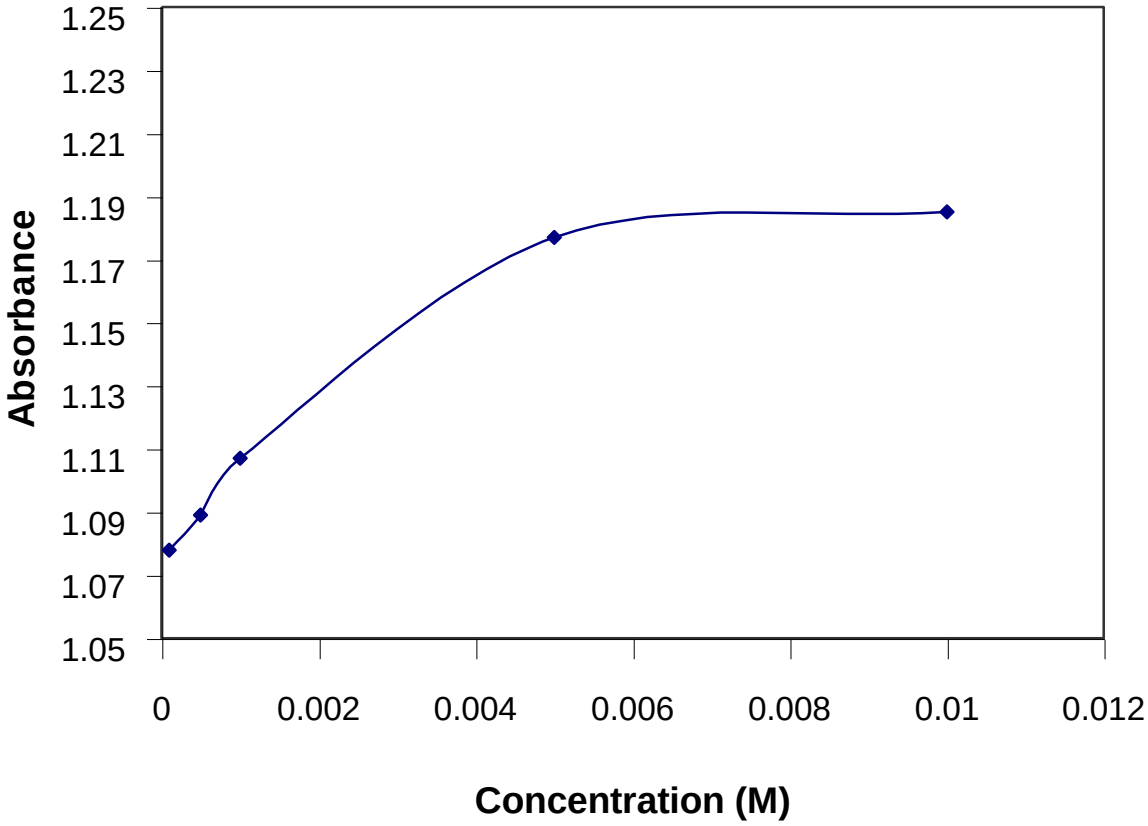


Figure 3.5: Turbidity absorbance vs. concentration of Ni^{2+}.

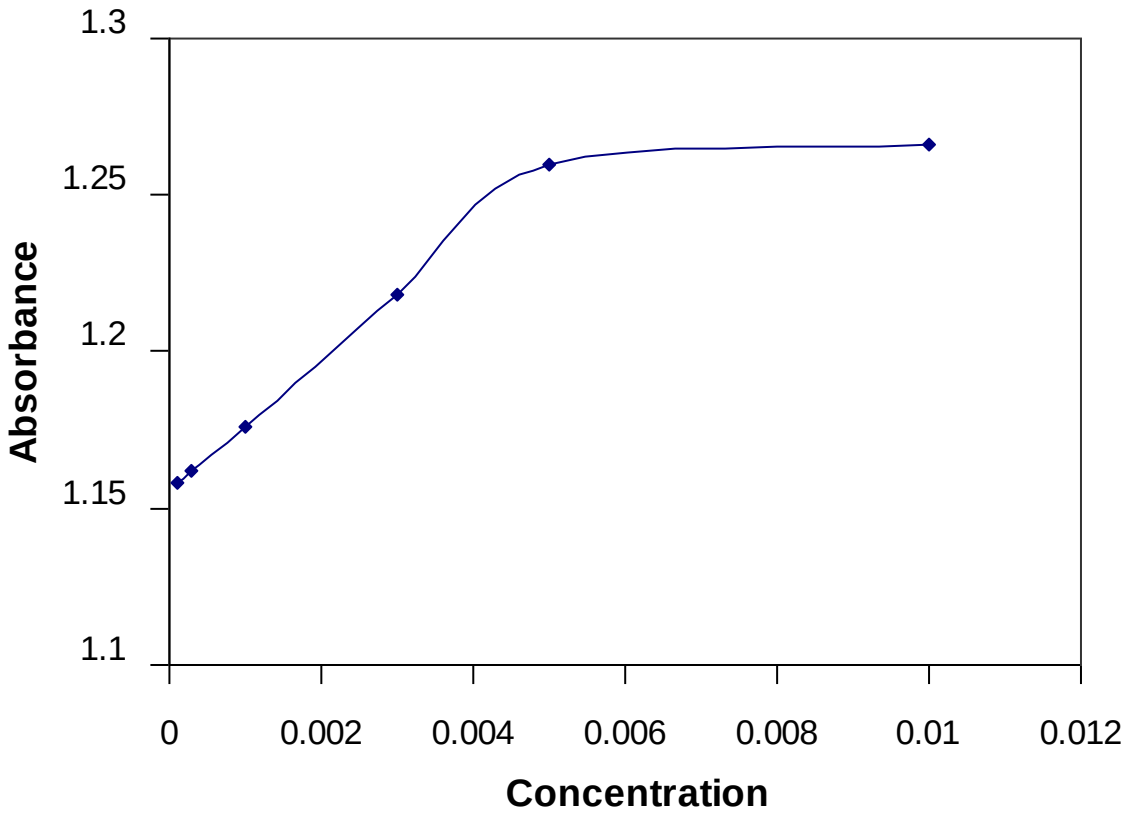


Figure 3.6: Turbidity absorbance vs. concentration of Cd^{2+}.

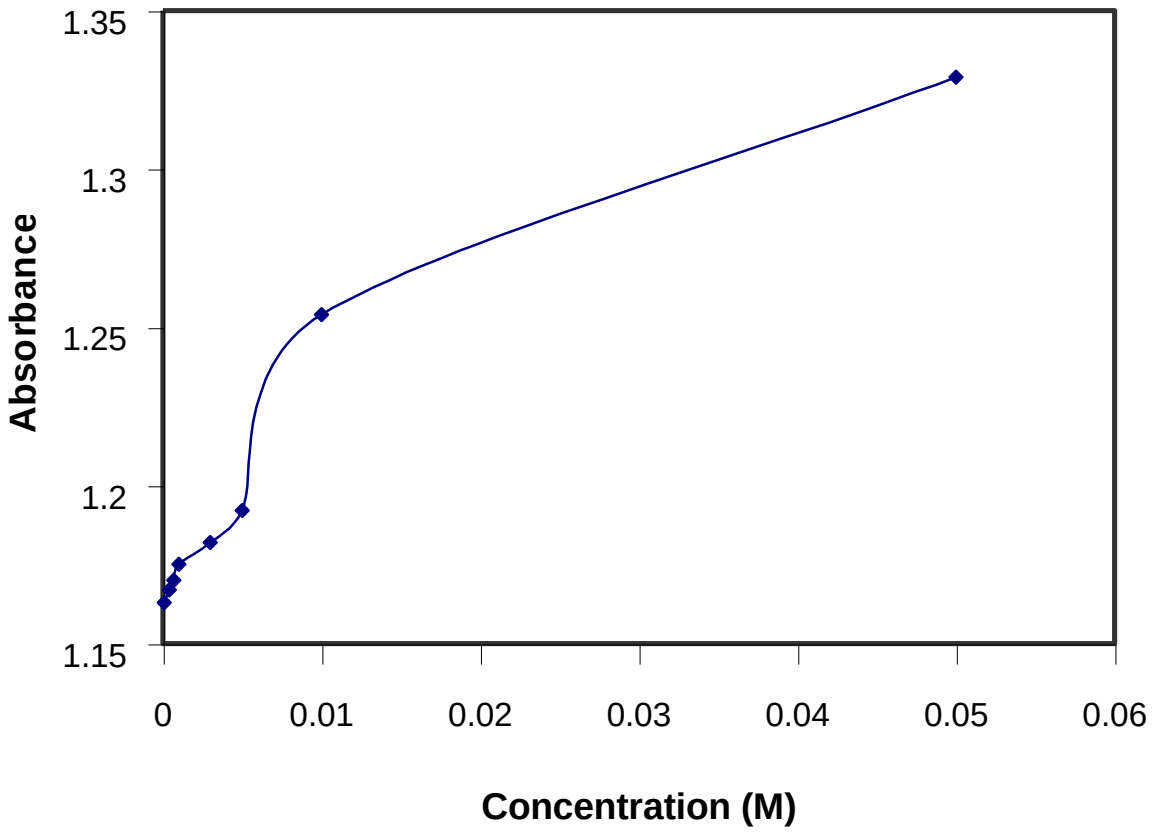


Figure 3.7: Turbidity absorbance vs. concentration of Pb^{2+}.

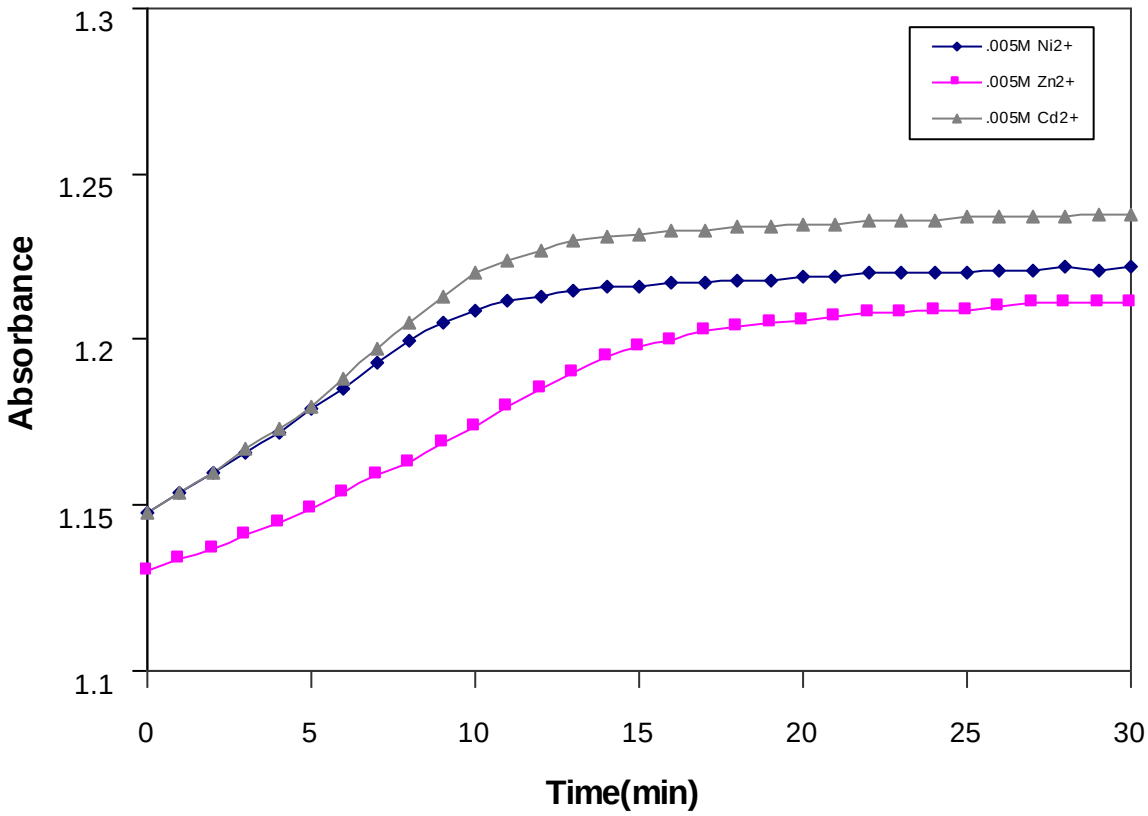


Figure 3.8: Absorbance vs. response time to Ni^{2+}, Zn^{2+}, and Cd^{2+}.

Figure 3.9 shows the turbidity absorbance vs. concentration of Ni^{2+} in a buffer solution at pH 6.9. When the sensing element was exposed to Ni^{2+} ions with different concentrations of solution at pH 6.9, the absorbance increased and reached its maximum value at 0.0008M, and then it decreased at higher concentration of Ni^{2+}.

3.4 Response to alkali and alkaline earth metals

The response of the sensing element to alkali and alkaline metal ions such as K^{+}, Mg^{2+}, and Ca^{2+} was tested. There was no significant change in the absorption spectra with varying concentrations of K^{+}, and Mg^{2+}. Concentrations measured at wavelength 800nm are shown in figures 3.10, and 3.11respectively. For Ca^{2+} metal ion, the absorbance increased with increasing concentration as a result of complex formation between Ca^{2+} ions and the deprotonated dicarboxylate group, which causing the polymer microspheres to shrink, since it is well known that dicarboxylate group binds with Ca^{2+}. Absorbance increased with increasing concentration of Ca^{2+} up to 5×10^{-3}M as shown in figure 3.12.

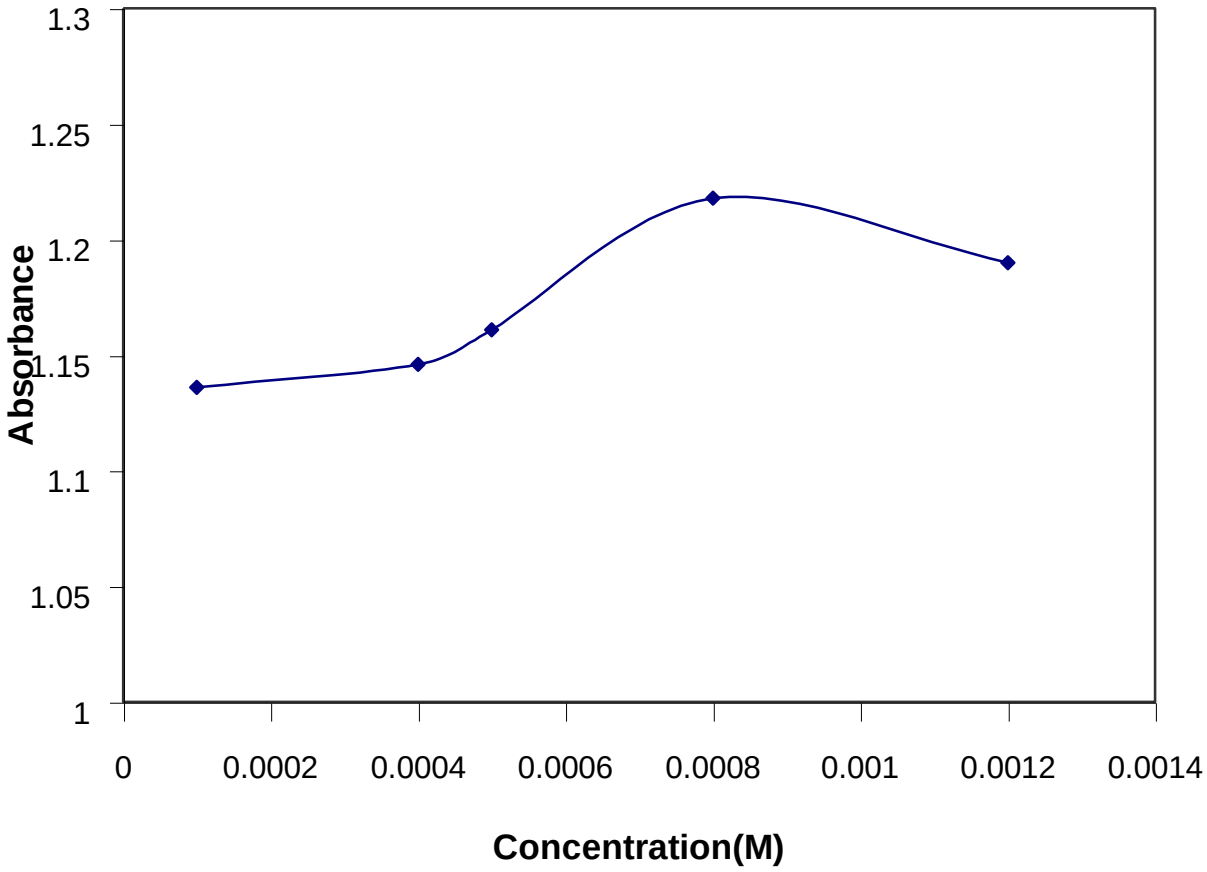


Figure 3.9: Turbidity absorbance vs. concentration of Ni^{2+} at pH= 6.9.

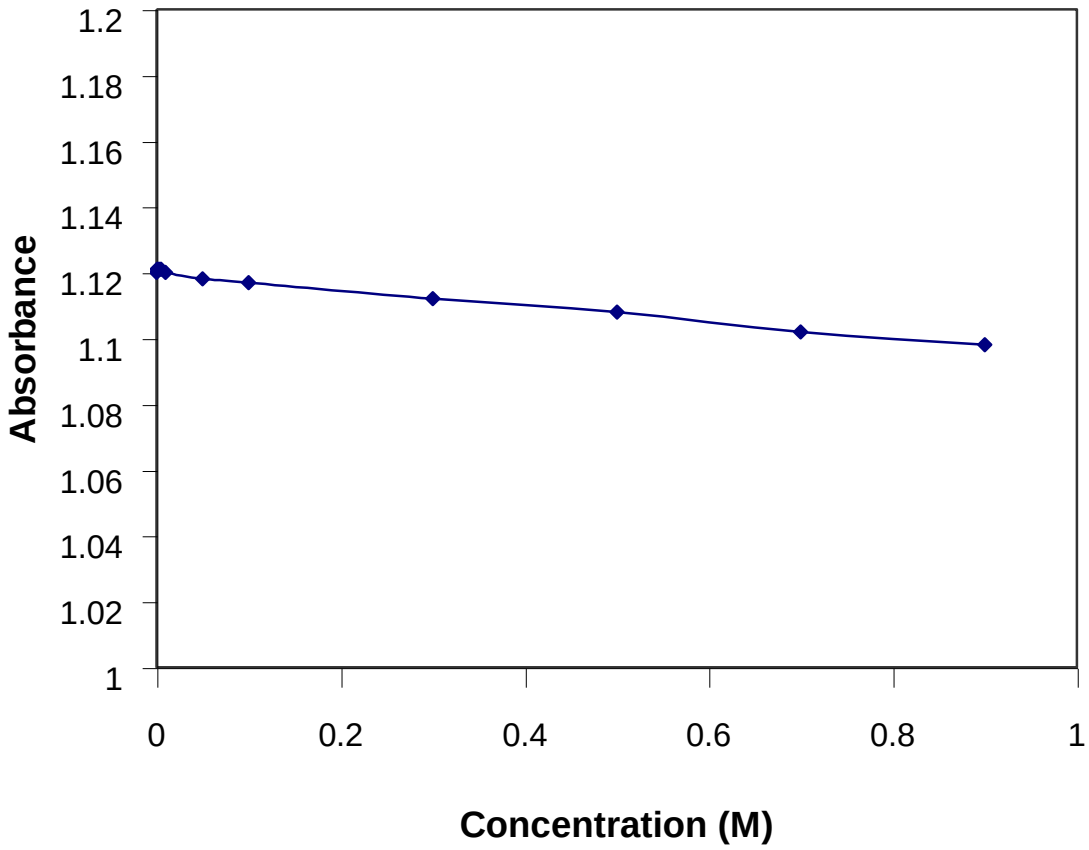


Figure 3.10: Turbidity absorbance vs. concentration of K^+.

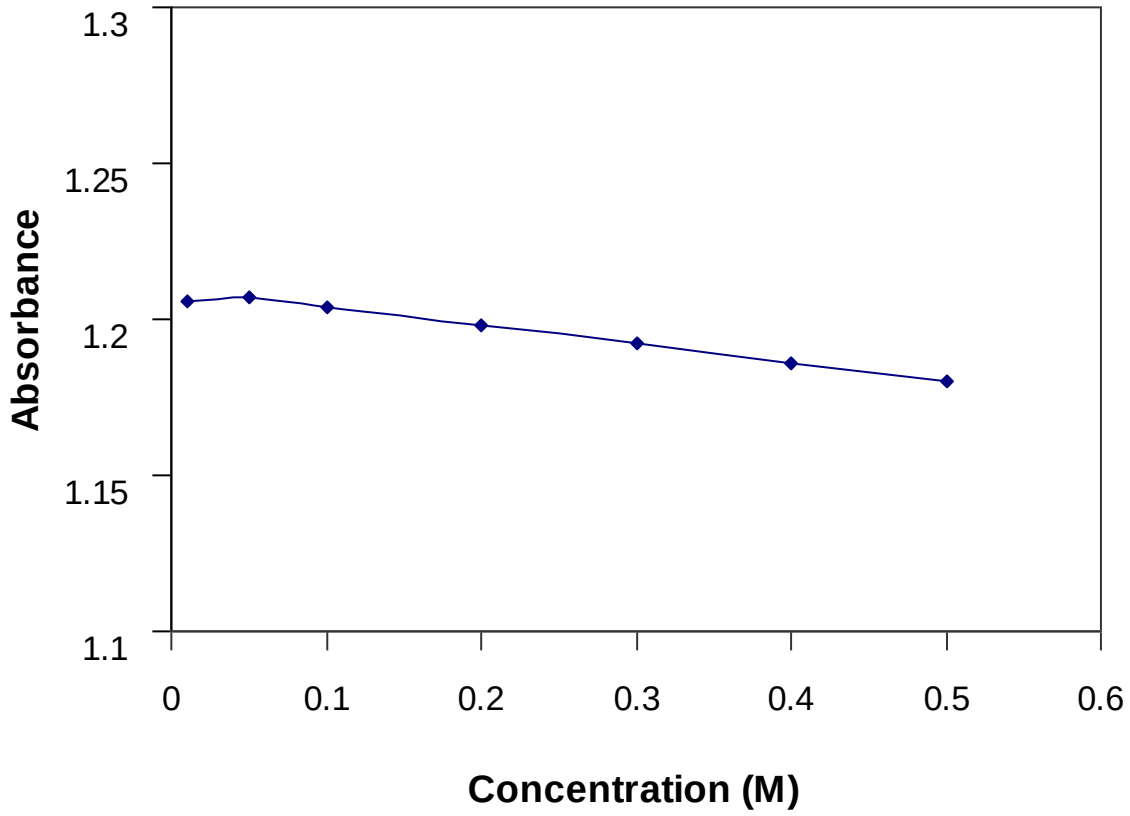


Figure 3.11: Turbidity absorbance vs. concentration of Mg^{2+}.

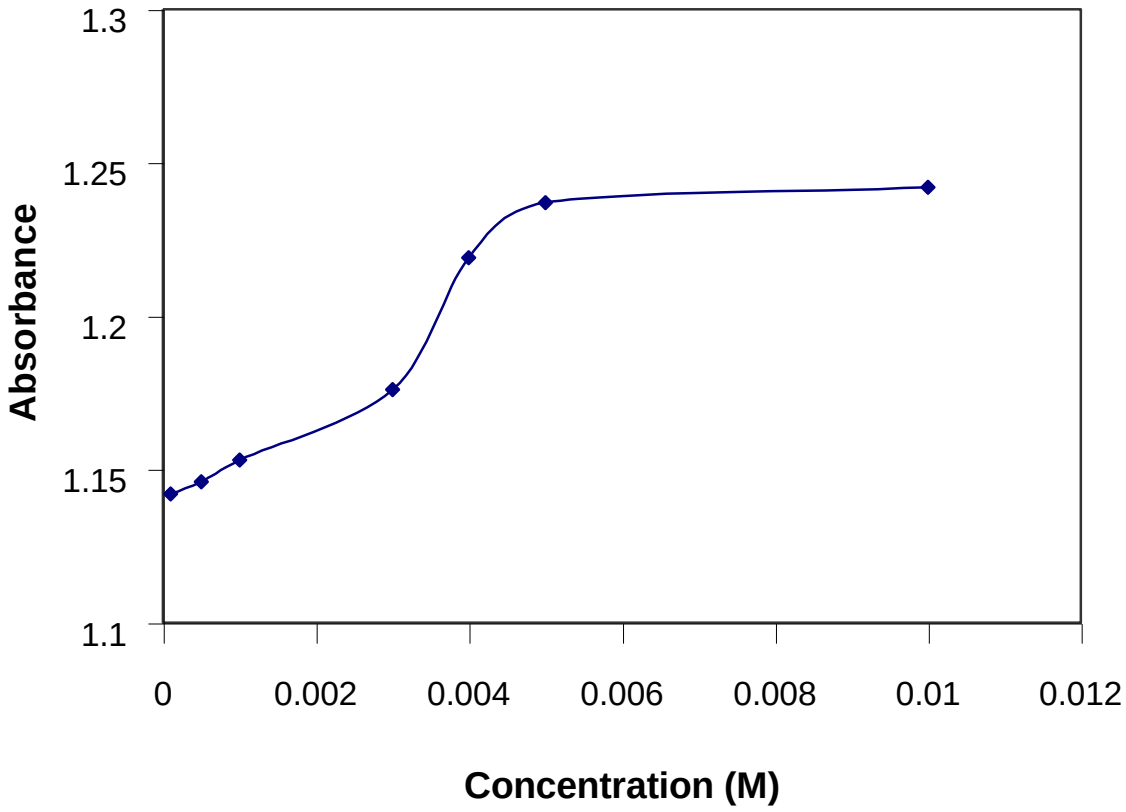


Figure3.12: Turbidity absorbance vs. concentration of Ca^{2+}.

3.5 Effect of temperature

The absorbance vs. temperature of 0.0002M Ni^{2+} in pH 6.11 is shown in figure 3.13. The absorbance increased slightly when the temperature was raised, especially above $30^{o}C$, results in shrinking. Shrinking causes a difference between the microsphere refractive index and the hydrogel refractive index resulting in an increase of the membrane turbidity that measured as absorbance.

3.6 Regeneration of the Sensing Element

After the sensor responded to any metal ion, the sensing element could be regenerated by the addition of 1.0M HCl. The metal ion was eluted, the absorbance dropped very fast, then it reached to a stable level. The fast drop in absorption by addition of HCl is due to the dissociation of metal ion from the polymer. Then the HCl was replaced with basic buffer of pH 9.13, the absorbance decreased more in a slow rate causing the polymer microspheres to swell since the dicarboxylate groups became deprotonated and repulsion occurred between adjacent negative charges.

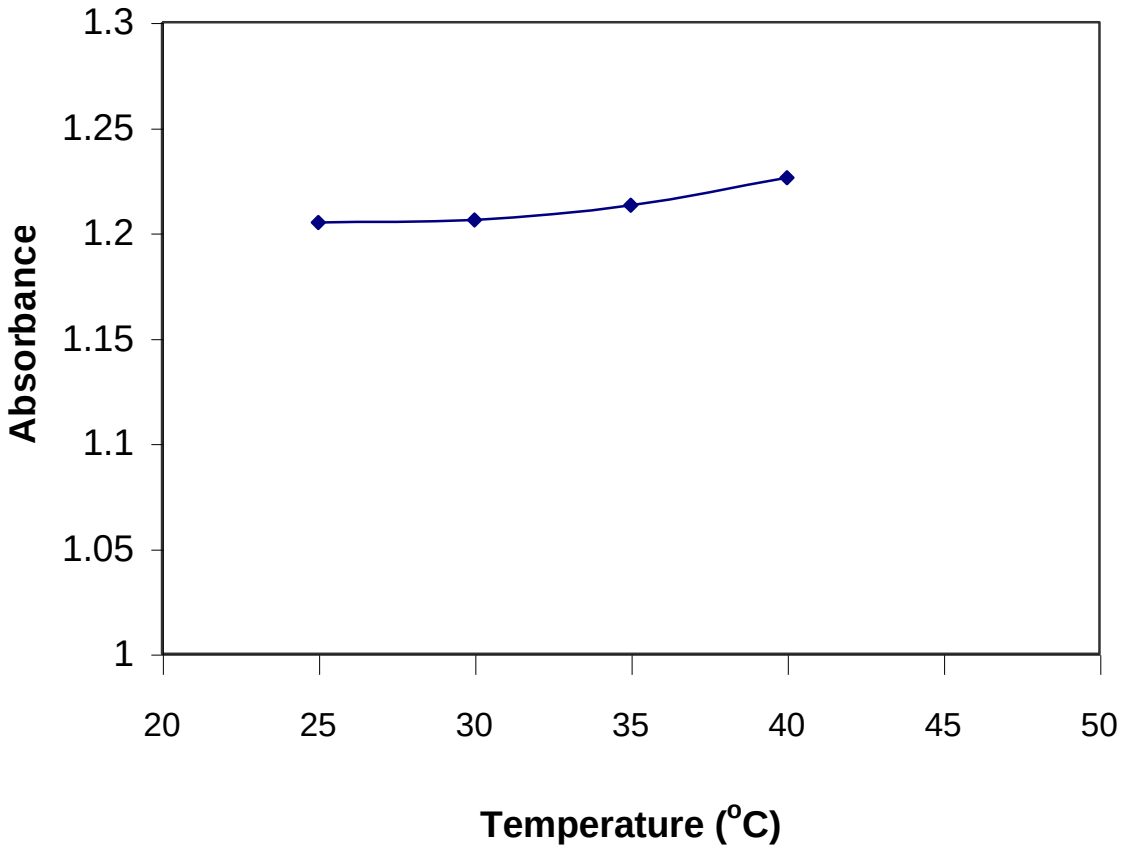


Figure 3.13: Turbidity of absorbance vs. temperature.

3.7 Lifetime of the sensor

The sensing element showed a reproducible response throughout my study. This indicates high mechanical and chemical stability. In order for the sensing element to have long lifetime of its hydrogel membrane, it should be kept in solution.

CONCLUSION

Chemical sensor based on swellable dicarboxylate functionalized polymer microspheres suspended in a hydrogel membrane can be used to determine different pH ranges and different metal ions with different concentrations.

The dispersed microspheres in a hydrogel membrane swell and shrink without any mechanical problems even after prolonged use, in addition to that this sensor has many advantages over other types of chemical sensors; it has good sensitivity, short response time, reproducibility, long lifetime, and low instrumentation costs.

This work could be further extended to modify this sensing element with other functional groups that are selective to different chemical species play a role in biological and environmental fields.

Our next goal is that we hope to achieve implementation of this chemical sensor to fiber optic technology.

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